Thermal Retro-Diels–Alder Extrusion of Sulphene from a Formal Sulphene–Arene Adduct

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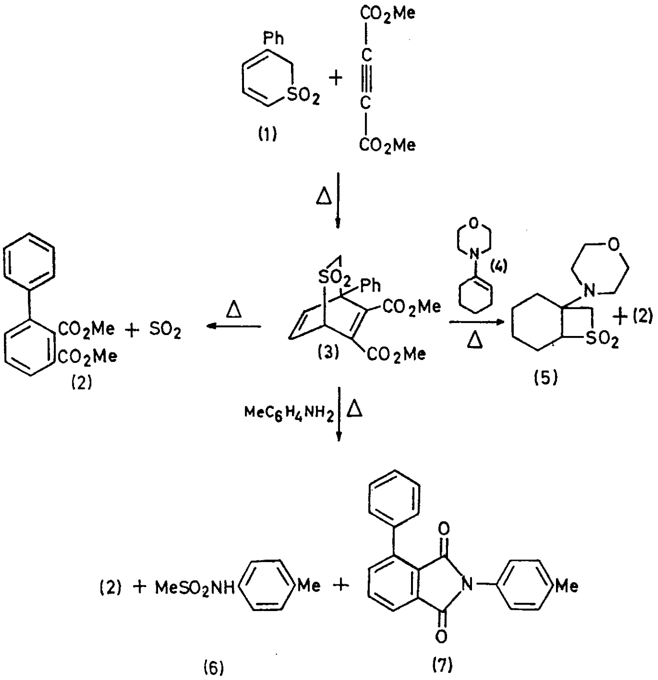
Summary Dimethyl 2,2-dioxido-4-phenyl-2-thiabicyclo[2,2,2]octa-5,7-diene-5,6-dicarboxylate (**3**) on heating gives dimethyl biphenyl-2,3-dicarboxylate (**2**) and sulphene, the latter being detected by trapping experiments.

Sulphene ($CH_2{=}SO_2$) and its derivatives are highly reactive intermediates of theoretical and synthetic interest.[1] They have not been obtained in a pure state but their existence has been shown by kinetic and product investigations[1,2] and low-temperature i.r. studies.[3] It is desirable to have a general method of generating sulphenes which does not involve the formation of by-products which themselves react with sulphenes. We have, therefore, investigated thermolysis of a formal sulphene–arene Diels–Alder adduct. Such a compound might be expected to decompose readily owing to the lowering of the activation energy for retro-Diels–Alder fragmentation by the stabilization accruing from the aromaticity of the incipient arene, and would yield a relatively unreactive co-fragment.

Dimethyl 2,2-dioxido-4-phenyl-2-thiabicyclo[2,2,2]octa-5,7-diene-5,6-dicarboxylate (**3**)† was synthesized by heating (**1**)[4] and dimethyl acetylenedicarboxylate at 140° for *ca.* 2 days. Thermolysis of (**3**) (220°, 5 min) gave a 95% yield of (**2**).[5] That sulphene was formed was shown by trapping experiments. Thermolysis of (**3**) (220°, 25 min) in the presence of enamine (**4**) gave a 38% yield of the sulphene enamine adduct (**5**)[6] and an 80% yield of the biphenyl (**2**). Thermolysis of (**3**) (325°, 1·5 min) in *p*-toluidine gave the sulphonamide (**6**) (52%),[7] biphenyl (**2**) (49%), and the derived imide (**7**) (17%)† (66% yield of total biphenyl products).



Sulphene and the co-product (**2**) evidently do not react with each other, but the fate of sulphene generated in the absence of a trap is not clear. When (**3**) was heated at 220 °C for 7 min, unchanged (**3**) (8%), the biphenyl (**2**) (81%), and sulphur dioxide [80 ± 10% of the sulphur from changed (**3**)] were formed. The formation of sulphur dioxide might suggest the possibility of the presence of a carbenoid species,‡ but thermolysis in the presence of cyclooctene gave no bicyclo[6,1,0]nonane. The unlikely possibility that sulphur dioxide arose from thermolysis of "sulphene dimer"[8] (1,3-dithietan-1,1,3,3-tetroxide) (which on high temperature flash thermolysis yields sulphur dioxide and ethylene[9]) was excluded by the absence (<5%) of ethylene from (**3**). Finally it was shown that the de-

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† This compound gave satisfactory microanalytical and spectroscopic data.

‡ Formation of such species from sulphenes has been looked for without success (*cf.* ref. 1).

composition of sulphene in the present case is different from that observed on flash thermolysis above 800 °C (which gives sulphur monoxide and formaldehyde[10]) since there was no sign of any formaldehyde in the thermolysate. A small amount of insoluble material is found on the walls of the tube; whether or not this accounts for the missing carbon has not been shown in our experiments, because of the intractability of the material and the small scale of the experiments.

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